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PETITION'S SUBJECT MATTER TITLE

METHOD TO IMPROVE THE HYDRODYNAMIC CHARACTERISTICS OF AGGLOMERATED PILES OF FINE CRUSHED ORES TO BE PILE LEACHED BY MEANS OF AN AGGLOMERATING AGENT CONTAINING A CATALIZING ELEMENT FOR COOPER RECOVERY REACTIONS FROM SULFIDE ORES.

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I/WE HEREBY DECLARE THAT THE DATA AS SHOWN AT THE PINK BOXES ARE TRUE, AND THAT I/WE KNOW ARTICLE 44 OF LAW No 19.039 ON INDUSTRIAL PROPERTY, AND THAT THIS DOCUMENT IS A FORMAL PETITION.

ATTORNEY'S SIGNATURE AND ID NUMBER
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PETITIONER'S SIGNATURE AND ID NUMBER

RECEPTION
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CHILE
INVENTION PATENTS

ORIGINAL

INSTRUCTIONS:

- 1.- FILL JUST THE PINK BOXES WITH BLACK CHARACTERS TYPED RATHER THAN HAND-WRITTEN
- 2.- PRIORITY IS UNDERSTOOD AS THE PROTECTION AS PREVIOUSLY REQUESTED, OR GRANTED, BY THE SAME INVENTION, USUALLY ABROAD.

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(54) Invention Title (330 characters maximum)

Procedure to agglomerate fine crushed copper ores by adding calcium chloride and sulfuric acid, and leaching procedure previous ore agglomeration.

(57) Abstract: (1600 characters maximum)

The heap leaching of agglomerated ores presents problems at high flow rates of irrigation, because agglomerates break up and reduce the pile permeability. This invention provides a procedure to agglomerate fine crushed copper ores consisting in adding calcium chloride at a rate of 5 to 25 kg/ton and sulfuric acid at a rate of 5 to 8 kg/ton into the ore agglomerator, thus producing an agglomerate of high mechanical resistance and piles with liquid permeability over 200 Darcy, and gas permeability exceeding 1000 Darcy. A procedure to leach agglomerates consisting in leaving the heap resting from 1 to 120 hours, then leaching with a flow ranging from 5 to 100 [l / (m²·hr)] for 1 to 200 days.

A 1.872% copper ore was agglomerated and leached with 20 [Kg/Ton] of CaCl₂ and 30 [Kg/Ton] of sulfuric acid, and 78% recovery was obtained in 110 days.

SPECIFICATIONS

INTRODUCTION

1.1. Scope

This invention refers to a copper hydrometallurgical discipline, which is related to the ore heap leaching. The heap leaching is an application field of the extractive metallurgical engineering that is booming in these days. In fact, most the new mining copper investment projects being implemented, or to be implemented in the near future in our country, are based upon the pile or heap leaching treatment¹.

In simple terms, pile leaching consists in percolating a reactive solution through an ore pile to extract the valuable metal, by dissolution, as the solution percolates. Once the valuable metal is dissolved in the solution, various techniques to get the metal from the solution can be applied. Said techniques, such as the solvent extraction, cementation or direct electro-winning, are now part of the standard practice in the hydrometallurgical industry.

To treat piled ores, a series of leaching processes are used by the industry, whether through licenses, or because they are public known :

1. Dump leaching
2. Heap leaching
3. Vat leaching
4. TL leaching
5. Piling ore, classified through fine splitting

On the other hand, and generally speaking, in all of the cases listed above except Vat Leaching, percolation is carried out by a technique known as trickle leaching, or non-flooded pile. This means that the solution is applied on the pile surface at a flow low enough for the solution to drain freely, just by gravity and without entirely filling the ore pores.

All the above processes have been successfully applied at industry level for several years.

The term fine crushing refers to those particle size distributions commonly obtained on a crushing closed circuit consisting of primary crushing, secondary crushing and tertiary crushing closed circuit in series with a screen, thus reaching distributions with a very controlled particle size where the largest one is generally -12,7mm, -9,525 mm or -6,35 mm, depending on the process requirement. The same particle sizes may be obtained in open circuits, and so is done sometimes. However, in those cases the particle sizes are not dimensionally controlled as in the previous case.

On one hand, the concept of agglomeration corresponds to a process through which the ore particles are bound together by forces generated by an external medium. Usually, said medium is water and the forces are spontaneously generated through liquid bridges and capillary tensions. Such forces may be strengthened by the presence of salts in solution, as customarily occurs, since the industry generally uses chemical reagents in agglomeration. Furthermore, these forces may be significantly increased by adding specific binders, thus improving the agglomerate properties as we will see later.

On the other hand, coarse crushing is understood as the material produced by an open crushing circuit, generally consisting of just a primary crushing, and sometimes followed by a secondary crushing, to obtain heterogeneous coarse particles whose size may range from 25,4 mm to 101,6 mm., differing from the other ones in that they cannot be submitted to an agglomeration process.

The above classification is arbitrary and it is only based upon the process operating features. The advantages or disadvantages of each of the alternatives are obvious. The sole objective of this classification is now focusing on the application field of this new invention.

This invention refers to a new process that uses the pile leaching technique for an agglomerate fine crushed ore, hence, related to section 4 of the above table.

Further this documents addresses the leaching process of a piled material as obtained from fine crushing and agglomeration using the trickle leaching technique, in order to explain below the novel aspects of the new process claimed.

1.2. A different approach to the problem

Pile leaching of a fine crushed material jointly with agglomeration and trickle leaching for copper oxidized ores was first applied at industrial scale by Sociedad Minera Pudahuel on July 1980 (TL Process). This process was protected by the Chilean Industrial License N° 32.025, until June 1996, when such license expired.

This procedure has a series of advantages that the other pile leaching techniques do not have. For this reason, the process was successfully applied in other ore mines in the country.

Even though the process was originally designed for oxidized ores, a subsequent development also carried out by Sociedad Mineral Pudahuel extended its application field to the treatment of sulfides copper ores of secondary geological origin.

This process, whose improvement was success arrived to the application of the bacterial leaching concept, to the original process, was called BTL Process.

Due to the close relationship between the TL and the BTL process with the idea to be patented now, it is necessary to briefly describe the most relevant features of this process, in the current status of the technique, both for oxidized ores and for copper sulfides ores. This methodology will facilitate the explanation of the fundamentals of the complex but novel ideas that will be exposed.

1.2.1. Oxidized Ores (T.L. Process)

In this case, corresponding to the original application of the technique, the objective of the fine crushing and agglomeration involves both a chemical and a physical aspect:

- Fine crushing allows to improving the kinetics of the leaching reactions by incrementing the reaction surface.
- Agglomeration takes place in the presence of concentrate sulfuric acid. This allows to attack the gangue throughout the pile homogeneously, as well as extracting an important portion of the oxidized copper contained in the ore. This, in turn, allows to use a solution with a low concentration of sulfuric acid in the subsequent irrigation procedure, thus reducing the consumption of this reagent without affecting the copper extraction kinetics.
- On the other hand, from a physical point of view, agglomeration allows to get good percolation characteristics, which is not the case in with non-agglomerated fine crushing ore pile.

In fact, the most relevant requirement for the pile leaching is that the resulting piling must be homogeneous. As a result of this, the leaching solution flow will be even throughout the pile length, and at all depths, that is, no solution channels or non leached sectors within the pile, will take place thereby producing lower copper recoveries and higher acid consumption.

This characteristic is not obtained with a non-agglomerated fine crushing pile because of the segregation originated during the loading of materials with a wide distribution in sizes.

In general, these materials tend to segregate coarser material at the pile slopes, finally originating a structure of oblique layers in the direction of the slope angle that will hinder the circulation of the leaching solution.

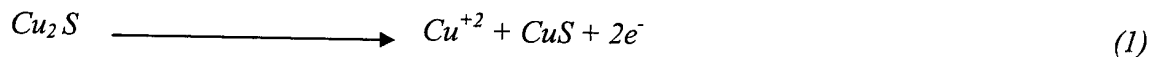
In second place, the kinetics of the pile leaching reaction is directly proportional to the flow of reagent through it, and therefore directly proportional to the flow of the solution containing such reagent. That is, the faster the solution goes through it, the shorter the time taken by the ore leaching. Now, the solution flow that may go through a pile depends on its permeability. Hence, the higher the permeability, the faster the copper extraction. On the other hand, the way in which agglomeration occurs determines the pile permeability, being its most relevant feature. These concepts have been presented in previous works².

1.2.2. Sulfides Copper Ores (B.T.L. Process)

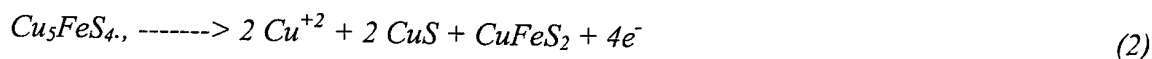
In this case, in addition of the above-mentioned characteristics, fine crushing along with agglomeration have an objective that is even more important: providing a physical medium to transfer of gas oxygen required for the sulfide ore oxidation reactions. Before explaining the effect of agglomeration over oxygen on a pile, the oxidation reaction in ore leaching must be briefly describe.

a) Oxidation reactions in sulfides ore

A sulfide leaching takes place due to the electrochemical oxidation of one of the elements constituting it. For instance, primary leaching of calcosine occurs thanks to the oxidation of the elementary copper contained in it, to the form of cupric ion, that is:



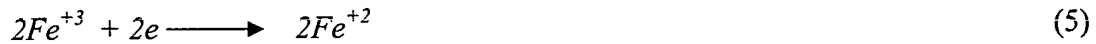
Similarly, for the first phase of bornite leaching:



On the other hand, the leaching of the coveline as contained in the ore, or obtained as a product of the calcosine reaction, takes place due to the electro-chemical reaction of the $S^{=}$ ion to elementary sulfuric, or, if oxidation is very strong, to the $SO_4^{=}$ ion:



Such oxidation processes occurred by the action of an oxidant, acting as electron acceptor, which is present in the solutions percolating the pile. For example, in the bacterial leaching of copper sulfide ores as mentioned above, the oxidizing agent is the ferric ion, which is reduced to ferrous ion according to the following reaction:



consuming the electrons generated in previous reactions.

Now, in a closed system, such as the leaching solution circuit of an industrial plant, the ferric ion will tend to disappear as electron acceptor as it is consumed due to the reaction with the sulfides. This means that, even though the ferric ion acts as a sulfide oxidizing agent, it could not be the final electron acceptor since it would end up consumed, leaving a final solution containing ferrous iron only, and stopping any subsequent sulfide oxidation.

This condition can be solved by externally adding to the plant a compound directly containing the ferric ion, or other oxidizer producing it. However, this solution is, in general, very expensive. Instead, the oxygen of the air can be used for this purpose, provided the physical characteristics of the pile permit it. This way, the ferric ion is permanently renewed according to the following reaction:



Acting as final electron acceptor.

The half-pile can also be described as a global reaction, where the oxygen reacts with the ferrous ion formed by the sulfide oxidation, reaction (5), as:



In summary, the chemical mechanism of the sulfide ore pile leaching can be summarized as follows. The oxygen in the air oxidizes the ferrous ion, which is present in the leaching solutions. In turn, the resulting ferric ion oxidizes the metallic copper (of the calcosine and the bornite) or the sulfuric (of the primary or residual coveline) thus reducing itself to ferrous ion. The ferrous ion formed oxidizes back with the oxygen, and the cycle continues until all the sulfide ore has been oxidized.

The chalcopyrite (natural or derived from the bornite reaction) has not been considered among the copper sulfides since the chemical mechanism as described above has not succeeded, to date, in releasing the copper contained in it, at a reasonable speed.

On the other hand, the oxidation reaction of the ferrous ion to ferric ion, reaction (7), can be catalyzed by the aerobic and heterotrophic bacteria: *thiobacillus ferrooxidans*. These bacteria can develop and grow in the ore leaching piles when the right conditions are present. When this takes place, the oxidation rate of the ferrous ion is dramatically increased. The process using this oxidation mechanism is generically referred as bacterial leaching.

The critical condition for this oxidation mechanism to occur is that the agglomerate characteristics allow the oxygen transference to oxidize the ferrous ion where needed. This is the most relevant foundation for the above-mentioned BTL process. This idea is also closely related to the new process that is now claimed, reason why it is described below.

b) Transfer mechanisms in agglomerated piles

The oxygen required to oxidize the ferrous ion, basically in the presence of bacteria, is mainly transferred by a mechanism of diffusion from the surface of the leaching piles as broadly proven³. That is, gas transfer follows a phenomenological pattern of the diffusion Fick's law type. In this case, diffusion occurs in a wet porous medium, whose porosity and tortuosity are related to the structure of the agglomerated material formed before starting the leaching process.

In the sulfide leaching, even more important than the agglomerate percolation is the pile's capability to allow an oxygen flow to pass through it. In this case, the oxygen is the most relevant reagent and the reaction kinetics basically now mainly relies on the agglomerate pile's capability to transfer the gas phase for the oxidation reactions, that is, on its porosity and gaseous permeability.

At this point, a development of the equations that describe this phenomenology is useless, as they have already been previously formulated. For the purposes of this presentation, it should be noted that the oxygen concentration in the gas atmosphere existing inside the pile decreases as one gets deeper, until being virtually nullified, or a threshold value given by the oxygen usage capability, in this case by the bacteria.

This means that, in general, a leaching pile consists of two zones: A zone where the oxygen concentration still allows the bacteria to survive, and the inner zone where, as a consequence of the shortage of oxygen, the bacteria either cannot survive or are not active. All rather, taking into account that the bacteria are the most relevant influence for the ferrous ion oxidation, a zone where the ferric ion is regenerated and consumed, and a deeper zone where the same is consumed only. On the other hand, the size of the oxidized zone is a function of the agglomerate characteristics.

This is quite relevant for the ore sulfide leaching process, as only a portion of the ferric ion generated in the oxidized zone is transferred to the pile non-oxidizing lower zone. The leaching capability of this portion of the pile is then restricted by the arrival of the ferric ion from the upper zone.

In summary, the issue here can be addressed to achieve the following objectives:

- a) Developing a process that will improve the transfer of the gaseous phase through the pile by means of an improvement in the agglomerate properties.
- b) Developing a process that will improve the oxidation rate of the solutions, taking maximum advantage of the difficult transfer of the oxygen in the gaseous phase.
- c) Developing a process that will improve the copper sulfides leaching kinetics.
- d) Developing a process that will not have any of the restrictions derived from the presence of a bacterial growth for the ferrous ion oxidation. In particular, the presence of chloride or other bactericides.

Consequently, in this invention, this is resolved as follows:

a) By improving the agglomerate properties, that is:

- Liquid permeability
- Gas porosity
- Gas permeability

by adding a binding agent in the agglomeration phase. This binding agent consists in an aqueous solution of chloride and calcium ions, but it may contain cations such as sodium, too. This solution puts in contact with the ore to which the sulfuric acid is added later.

b) By changing the composition of the leaching solution:

The chemical composition of the above-mentioned binder allows us to obtain a leaching solution whose characteristics are different from those used in the bacterial leaching. Its main advantages are:

- Oxidation rates higher than those obtained with bacteria
- Capability to form copper complexes as cuprous ion

c) By modifying the morphology of the reaction product layer.

The presence of a high level of chloride in the agglomeration phase derived from the binder added, promotes an intense oxidation reaction of the copper sulfides. The above has two consequences:

- A fast extraction of copper sulfide in the agglomeration. Similar to that obtained in the agglomeration of copper oxidized ores.

- The formation of elementary sulfur as a crystal, thus facilitating the diffusion of oxidizing ions inside the ore's particles.

d) By using salty waters.

Because this process does not use bacteria in oxidation reactions, using water containing chloride to replace the normal loss in a leaching plant becomes an advantage, as it partially reduces the amount of binder to be used. In many places in this country, this is the only resource available.

1.3 State of the art.

This section of the presentation basically consists in reviewing the literature in terms what is known to this respect against the conceptual ideas of the basic aspects of the new process. That is:

- Agglomeration and binders
- Sulfide leaching in chloride medium
- Solution oxidation rate

This review allows us to demonstrate by comparison the novelty of this invention, even the three aspects as considered on an individual basis. However, even though each issue is novel in itself, it should be noted that according to this proposal, the invention process will best work when all the above-indicated actions are applied at the same time.

All references made in this work are duly ordered and at the disposal of the expert as appointed by the Licenses Office, in order to assist him/her in his/her bibliographic search.

1.3.1. Agglomeration and Binders

Using agglomeration to improve the percolation properties of ores obtained from fine crushing has been broadly studied, basically in the field of gold ore pile leaching. In this case, the traditional technique of agglomeration consists in adding limestone and Portland cement along with water to obtain, on the one hand, an alkaline environment for the subsequent leaching with sodium cyanide, and on the other hand, to produce an agglomerate that is resistant to the flow of a percolating solution, through the addition of cement, acting as natural binder.

In the case of oxidized or sulfide copper ores, that is, in TL and BTL processes as mentioned above, agglomeration occurs with water and sulfuric acid. In this case, the use of cement or limestone is discarded as both materials react with sulfuric acid and, therefore, lose their characteristics as binding materials. The above, without considering the disadvantage of the use of acid involved in the attack of these species.

When fine crushed materials are used without additives, the percolation capability of a pile is very little, mainly due to the segregation between the fine and coarse particles that takes place during the pile loading operations⁴⁻⁶. For eight years, the U.S. Bureau of Mines developed a process to improve the gold ore recovery by improving its percolation conditions^{7,16,17,20}. The first works as performed by this research team set the first intent in the agglomeration technique for precious metal ores through the above-indicated additives.

On a parallel basis and from the perspective of private companies, similar conclusions were reached by Chamberlin^{6,14,15} even though from a more practical point of view, the references of which were reviewed in detail by this author in terms of the industrial methods to get the agglomerates.

In 1982, following the application of the SMP TL process in Chile, Phariss and Pcmichelle⁹ make a summary of the technical and economic advantages of the agglomeration, and it is interesting to note that the observations made by these authors are still valid, even for copper ores.

Darwin, Arizona¹⁰, shows an interesting industrial application of the agglomeration process as descriptile for silver ores. A general description about the importance of the agglomeration and percolation stage parameters is given under references^{8,11,18}. It is interesting to note Lastra & Chase's statement under page 1538 of reference¹¹. "Until a solid agglomerating reagent not soluble in sulfuric acid shall be found (the most widely used leaching means), the agglomeration of uranium and copper ores will have a limitation in the size ... of particle." The current work seems to have this dilemma resolved.

Most of these references deal with the application of agglomerating agents useful for the gold ore leaching. Until then, the single use of the agglomeration process in the copper ore hydrometallurgy was the one practiced by SMP in its Lo Aguirre and La Cascada operations. As already stated, it consisted in an agglomeration with water and sulfuric acid. In 1985, the South African Mintek institute¹³ completed a pioneer work, which was aimed at finding a way to agglomerate the finely disseminated copper ores, such as flotation or other products, to be leached in stockpile.

In this work, the author used both organic and inorganic additives as agglomerating means. Given its importance for the present discussion, it should be mentioned the inorganic additives used there:

- CALCIUM SULPHATE:

Various forms of natural and synthetic CaSO_4 .

Lime and sulfuric acid.

Limestone and sulfuric acid.

Slaked lime and sulfuric acid.

- CLAYS:

Bentonite.

China clay.

An ordinary type of loam.

- FERROUS SULFATE

In 1974, this compound was registered in South Africa as agent to agglomerate sulfide concentrates. South African Pat. NQ 742.260.

- PORTLAND CEMENT.

- SILICATES

Silicic acid

Sodium metasilicate

Sodium silicate

Sodium silicate and lime

Sodium silicate and zinc oxide

Sodium silicate and sodium carbonate

Sodium silicate and silica powder

Sodium silicate and sodium silico-fluoride

It is remarkable that none of these additives affect the matter or the concept of the recovery of the actual idea.

Although several organic additives were tested in this work, they by no means affect this recovery, so they are not listed.

The most interesting thing to note in that article is that the author concludes that the most promising additive among the inorganic additives being used is the mixture of calcium hydroxide with sulfuric acid to form calcium sulfate "in-situ". This calcium sulfate or plaster finely distributed acts much more effectively as bonding product among the finer and the coarser particles than when it is added as a compound.

Nevertheless, from our point of view, this reactive system shows a clear deficiency, as any added lime reacts with sulfuric acid, and therefore, it consumes it, whether directly added in the agglomeration or coming from the leaching acidic solution. This disadvantage disappears in our invention, without the loss of the concept.

Then, for oxidized copper ores, the Chilean patent 36.009 of 1988 proposes a mixture of:

Water with NaCl plus sodium silicates.

Lime or limestone mixed with the ore.

Sulfuric acid.

In other words, the only difference with some of the cases studied by MINTEK is the addition of NaCl.

On the other hand, the reference¹⁹ refers to a system that is currently being analyzed as an alternate technology in some plants of the country and which, on a broader sense, corresponds to a process consisting in eliminating the fines before loading the stockpile, as mentioned under point 1.1. In this respect, there is a Chilean patent (NQ 35.803 from Codelco) and a patent request NQ 872-94 from Compañía Minera Zaldivar) to eliminate the use of agglomerates, which do not affect the process herein discussed.

To complete this revision, a brief presentation is made of other additives used in agglomeration, only with a view to emphasizing that these products have nothing to do with this original idea either. The already mentioned Mintek¹³ Institute tested the following organic additives: Agar, gelatin, guar gum and gum Arabic. Uranium ores have shown some usefulness at using clay stabilizers before and after beginning the leaching. A number of inorganic reagents are known for this purpose, such as aluminum hydroxides, liquid zircon oxychloride solutions, and some aluminum chlorides¹². A cationic polymer²¹ has been found that produces a similar effect.

More recently^{22,23}, a number of organic commercial products have appeared to assist in the agglomeration. They are based on the polyacrilamide chemistry, except for the Leach-It (22) compound, which is based on the lime, as in the Mintek research.

This wide bibliographic revision has been aimed at showing that the system herein proposed is novel, because the compound is more than just an agglomerating product; since it is also a reactive product.

1.3.2. Leaching of Secondary Copper Sulfides in a Chloride Environment

In general, the copper ore hydrometallurgical treatment may be divided into two (2) major areas: direct ore leaching and concentrates leaching. As already stated, the direct ore leaching is carried out in stockpiles by using one of the above mentioned techniques, i.e., dump, heap, vat, TL leaching, and fines separation. The chemistry involved in these processes is invariably based on the attack of the sulfides by means of the ferric ion, which is continuously renewed by the ferrous ion oxidation with air, generally assisted by bacteria. These processes are conducted in an environment mainly consisting of sulfate anions.

In some cases, the sulfate environment may be contaminated with chloride from the ore, particularly in the leaching of atacamite ores or because it comes from the waters used in the leaching. The water may be from salt deserts, the sea or salt rivers. For the oxidized copper ore leaching process, the presence of chloride in the leaching solutions is not a problem; in fact, it is advantageously used that way, for example, in the Mantos Blancos process²⁴.

For the sulfide leaching, however, the presence of chloride in high concentrations inhibits the bacterial growth. For example, it has been found that a concentration of 7 [g/l] of chloride in a sulfuric solution reduces the ferrous ion oxidation rate by 58%, while with a concentration of 14 [g/l], the reduction is of

92%²⁵. On the other hand, (Weston et al)²⁶, who worked in a leaching by agitation with ores from the Chilean Zaldívar mine, obtain satisfactory copper mining results, although the chloride concentration was 3 [g/l]. Vorreiter and Madgwick²⁷, working in ore columns, found a complete inhibition of the bacteria when the chloride concentration reached 21 [g/l] (very near the sea water). In addition, these authors find that the bacterial leaching is only partially reestablished even after a thorough washing of the stockpile contaminated with chloride, probably, according to them, due to the persistence of small residual quantities of chloride in the stockpile. This apparent contradiction with Weston's result is explained by the fact that the effect of the chloride on a pad leaching seems not to completely eliminate the bacterial growth, but prevent its bonding to the ore surface.

Another interesting fact found by Vorreiter and Madgwick²⁷ is that the presence of NaCl improves the soluble copper mining.

On the other side, it has been discovered that, in the absence of bacterial leaching, the presence of chloride in the leaching solutions permits to leach an important part of the sulfides contained in mixed copper ores²⁸. This is noted on an industrial basis, for instance, in the Chilean El Lince mine, a plant originally designed for the treatment of ores oxidized with sea water which, when used for the treatment of mixed ores, recoveries of about 45% are obtained for the sulfide species, without bacterial leaching.

This same principle has been used by the Broken Hill company in Australia^{29,30,31}, for the recovery of copper from Cu-Pb mattes obtained as an intermediate product in its lead smelter. In this case, the leaching consists in the oxidation of the copper-lead matte with a leaching solution formed by an acidic chloride-sulfate and oxygenated mixture obtained by injecting oxygen produced in the same plant. The conditions for this leaching are: a temperature of 85°C and a chloride concentration of 20 to 25 gpl added as NaCl. It is interesting to note that the origin of

this process is in the idea of using the matte leaching in a chloride environment and, on the other hand, the sulfate ion is used to precipitate the lead as lead sulfate.

Based on the principle used at Broken Hill, Cheng and Lawson^{32,33} study the kinetics of the particle leaching with a size of particles of $-75\ \mu\text{m}$ of synthetic chalcocite and coveline in a sulfate-chloride environment oxygenated by injection of pure oxygen in an agitated reactor. The leaching conditions are similar to those used in BHAS, say, 85°C of temperature, a chloride concentration of 18 gpl, sulfuric acid at 25 gpl and a pressure of one (1) atm of oxygen. The main conclusion of these authors is that the role of the chloride ion apparently consists in breaking the sulfuric crystalline layer formed on the particle. This was confirmed in the works of Majima, Awakura and Hirato^{34,35}, by leaching chalcopyrite ores with iron chloride and copper chloride.

On the other hand, Fisher et al^{36,37} compare the chalcocite dissolution in a solution oxygenated both in a chloride and a sulfate system. These authors find that the kinetics of the dissolution of the first stage of the chalcocite is seventy (70) times faster in the chloride environment than in the sulfate environment. They state that this effect is due to the formation of the complex: CuCl_3^{-2} . These authors tested concentrations up to 35 gpl of chloride and found a reaction kinetics proportional to this concentration; nevertheless, they find that the kinetics of the second stage of the chalcocite leaching is independent from this concentration and only as a function of the temperature.

Finally, there is a number of works about the leaching of the chalcopyrite in a chloride environment. These works are invariably related to the leaching of concentrates by agitation, and therefore, have no relation with this invention.

1.3.3. Solution Oxidation

In the conventional hydrometallurgical treatment of the sulfide copper species, always conducted in a sulfate environment, the copper sulfides are oxidized as a result of the presence of the iron ion. This ion, on the other hand, is regenerated by the oxidation of the ferrous ion with air and

Also, the natural oxidation of the ferrous ion is relatively very slow and, if there is no an acceleration mechanism, this stage becomes the controlling agent of the sulfide ore leaching rate.

On the other hand, in a sulfate medium with moderated concentrations of the $\text{SO}_4^{=}$ ion, the presence of bacteria taking advantage of the ferrous ion oxidation rate is possible. In a pile, as already mentioned, the oxidation rate of the ferrous ion not only depends on the kinetics of the oxidation reaction but it also depends on the agglomerate properties.

In simple words, it is not the same oxidizing the ferrous ion in an agitated reactor than in an ore pile, agglomerate or not, where the oxygen transference phenomena, from the gas phase to the reaction place where this latter is consumed, become the most important mechanisms.

For a normal agglomerate, obtained in the way descripile above and without oxidizing bacteria, the oxidation rate of the ferrous ion ranges from 0.5 to 1.0 [$\mu\text{g/g}\cdot\text{Hr}$], expressed as oxygen consumption in micrograms, per gram of agglomerate, in one hour. If, on the other hand, the conditions are suitable for the bacterial growth, such rate can range from 15 to 20 [$\mu\text{g/g}\cdot\text{Hr}$], that is, 20 times higher. These values have been obtained in tests performed at laboratory level. At an industrial plant, the rates range between these two values. These results clearly show the advantages of the bacterial leaching.

Also, it is known that the oxidation kinetics of the ferrous ion, when taking place in the natural way, can be improved by a little bit over three times in the presence of a cupric ion³⁸.

A totally different condition is obtained for the oxidation rate of the cuprous ion with oxygen in comparison to the oxidation rate of the ferrous ion. The oxidation rate of the cuprous ion can reach 1,000 times higher than that of the ferrous ion in water³⁹. However, the cuprous ion is not thermodynamically stable in a solution typical to the leaching, that is, based on a sulfate medium.

To take advantage of this unusual oxidation kinetics, it is necessary to find the conditions to thermodynamically stabilize the cuprous ion. This can be done by using a medium to form complexes for the cuprous ion, such as the chloride anion, among others. In a chloride medium, and depending on the amount of chloride present, the cuprous ion can form a variety of species, such as: CuCl_2 , CuCl_3^{2-} , and CuCl_4^{3-} . In the previous reference, the authors consider that the oxidation of the solution depends on the concentration of the chloride ion, as well as on the pH of the solution.

A thorough review of the literature about the oxidation of leaching solutions shows that the systems on which the kinetics studies have been conducted are the following:

1. Oxidation of Fe^{+2} in sulfate medium
2. Oxidation of Fe^{+2} in sulfate medium catalyzed by Cu^{+2}
3. Oxidation of Fe^{+2} in chloride medium
4. Oxidation of Fe^{+2} in chloride medium catalyzed by Cu^{+2}
5. Oxidation of Fe^{+2} in chloride medium

Even though the oxidation kinetics of the Fe^{+2} or the Cu^{+2} ion depends on several factors, a close summary of the average values of the initial leaching kinetics for the normal conditions as indicated can be shown in the following table:

TABLE No 1: OXYGEN OXIDATION KINETICS IN THE MEDIA INDICATED

Conditions:

PH = 2

$[\text{Fe}^{+2}] = 2.8 \text{ [g/l]}$

$[\text{Cu}^{+}] = 6.4 \text{ [g/l]}$

SYSTEM	RATE [G/L*Hr)	RATIO
1	0.00816	1.0
2	0.02640	3.2
3	0.00576	0.7
4	0.71996	88.2
5	2.63984	323.5

In the bibliographic review made, no reference related to the study of the kinetics of the simultaneous oxidation of Fe^{+2} and Cu^{+} , in a sulfate-chloride medium, has been found.

2. DETAILED DESCRIPTION OF THE INVENTION

2.1. Invention Abstract

This invention makes use, in a new way, of all the theoretical concepts involved and discussed in the previous sections. The original idea can be summarized in a very simple form: a fine crushed ore, before being pile leached, is subject to an agglomeration process where, by means of a suitable mixing equipment whose design is standard in the ore leaching, the ore puts in contact with water, calcium chloride, or a chloride, calcium, and sulfuric acid solution, inducing during the agglomeration the following simultaneous effects:

- Simultaneously producing calcium sulfate, in situ, which acts as a second binding agent of the ore particles, thus improving the physical characteristics of the agglomerate.
- Reducing the SO_4 ion contents, replacing them for chloride ions.
- Making the cuprous ion to form by forming complexes with the chlorine ion from the agglomerating compound.
- Incrementing, due to the presence of the cuprous ion, the oxidation rate of the solution to form the ferric ion, from the oxidation of the ferrous ion as generated by the acid action on the ore.
- Attacking the sulfide ore particles by means of the ferric ion so that, due to the presence of the chloride ion, the reaction product formed, elementary sulfur, is permeable to the oxidizing agent.

- Distributing the sulfuric acid consumption among the following reactions: a) consumption for the gangue reaction, that is, dissolving the cations and reacting with the calcareous species, b) consumption for Cu^{+2} from the soluble ores, c) consumption for the solution oxidation, and mainly d) consumption for oxidation of the copper sulfides.

Once the agglomerate formed is allowed to rest during the time required for all the effects above mentioned to be completed, the agglomerate is pile leached with an irrigation solution containing, at least, the following elements:

Chloride Ion: in a concentration high enough to allow the presence of the cuprous ion, and consequently, the continuous generation of the ferric ion. The chloride ion concentration as required for this process is fairly higher than those of the applications mentioned in the bibliographic review.

Cooper: in a concentration enough to guarantee the presence of the cuprous ion, in the amount as required for the oxidation of the ferrous ion, catalyzed by the same.

Ferrous Ion: in an amount enough to oxidize to ferric ion, which acts as an intermediate electron acceptor for the oxidation of the copper sulfides.

Acid: in an amount enough to satisfy all consumption, and mainly, a surplus for the oxidation reaction..

Furthermore, the pile should be able, due to the agglomerate properties, to allow the oxygen transference from the gas stage, at the rate as required by the sulfide oxidation reactions.

It should be noted that, none of these elements except the acid should be externally added during the process. The concentrations obtained for these elements result from the mass balance of the

solutions as reached by the plant when operating in steady state.

The chlorine ion from the CaCl_2 , used as agglomerant but at invention realization level, can be regenerated during the process as a chloride and calcium solution.

To obtain a copper concentration high and controlled enough, the solution can be recirculated, as seen in the section Preferred Realization of the Invention.

Finally, the ferrous ion derives from the acid reaction with the gangue of the ore.

Once the copper extracted from the ores is in the leaching solution, said copper can be obtained by means of the standard methods known at hydrometallurgical level. That is, solvent extraction, cementation, or direct electro-winning. This last part of the recovery of the copper obtained is not part of the purpose of this invention.

Next, the basic concepts of the process are described in detail, and the way of implementing them in an industrial practice is explained.

2.2. New Agglomeration Process

The idea involved in this process came up unexpectedly. In fact, during the study of a sulfide ore containing excessive clay material, which **did not response** to the traditional TL agglomeration, that is, the addition of water and sulfuric acid only. An attempt to solve the situation was made by using a series of agglomerants such as those discussed, as well as calcium chloride, this latter for the purpose to form CaSO_4 -in situ- acting as binding agent for the finest particles.

The idea of using CaCl_2 to agglomerate was new since, with a sulfide ore, it was previously known that the presence of chloride would prevent the presence of bacteria. So, it was concluded that if the use of CaCl_2 proved to be successful, a thorough wash with fresh water would be necessary before attempting a bacterial leaching.

An unexpected condition was found when obtaining the first leaching effluents of these agglomerates. They had a high copper concentration. From that point and on, the project turned into the search of the causes of this behavior for the purpose to develop and optimize a new method, of inventive level, likely to be applied at industry level, making use of this property. The outcome of this effort is shown below.

As it was found out later, the most significant fact is the phenomenon taking place during the curing, that is, during the agglomerate rest. The same phenomenon takes place in the leaching, even though in other circumstances.

2.2.1. Effect on the Agglomerate Properties

The first beneficial effect of the addition of CaCl_2 is common to all the agglomerants used in the pile leaching process, and consists in the fact that this procedure improves the percolation properties of the liquid. In all the agglomeration methods known, the improvement of the percolation properties of a pile derive from the formation of an interfacial compound, organic or non-organic, at the surface of the agglomerate ore particles.

As an agglomeration method, adding CaCl_2 is aimed at forming calcium sulfate, in situ. This way, as already observed by MINTEK at the reference mentioned, the plaster formed has better sticking properties than the calcium sulfate externally added, since a better distribution of the reagent among the ore particles is obtained

In the blend tested by MINTEK, lime or limestone is added along with the sulfuric acid to form calcium sulfate, according to the following reaction:



Against the process hereby proposed, this reaction shows two major disadvantages, on one hand, this is a sulfuric acid consuming reaction, and on the other hand, since lime is not soluble in water no matter how fine may be, the reaction is always heterogeneous.

Other major difference is that this reaction also leaves the sulfate ion solution that would be obtained if no agglomerant was added, since adding acid enough for the consumption derived from the leaching reactions is required.

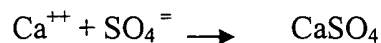
Whereas, adding CaCl_2 along with sulfuric acid to the agglomeration, produces a reaction forming plaster without acid consumption. This way, all the sulfuric acid protons remain available for really useful reactions, such as those of the copper leaching. In this case, the reaction can be written as:



that is, the reaction only produces a partial exchange of anions between sulfates and chlorides. This reaction takes place until all the calcium precipitates as plaster, and consequently, the final proportion of chloride ions to sulfate ions will be a function of the amount of calcium chloride added.

The other different effect against the addition of Ca(OH)_2 , is that, in this case, the CaCl_2 can and must be added already dissolved in water, taking advantage of the high solubility of this salt in water. This way, the previous reaction is homogeneous. This fact is considered key for the agglomeration process, since in this case, the plaster crystallizes more homogeneously than a solid compound as the lime or limestone, which should be thoroughly mixed with the ore to obtain some similar degree of homogeneity.

The real mechanism of the reaction is simpler, the calcium ions in solution react with the sulfate ions from the sulfuric acid:



This way, the element acting as agglomerant is the calcium only, and the use of calcium chloride is due that this salt is very soluble in water.

As already mentioned in the introduction of this presentation, one of the main purposes of the new process is improving the hydrodynamic properties of the agglomerate, in terms of:

- Liquid permeability
- Gas permeability
- Gas porosity

To determine the effect of adding CaCl_2 on the physical properties of the agglomerates, a fine crushed ore containing some 8% with a fine fraction under $-100\#$ was agglomerated with 30 [kg/Ton] of acid, and 90 [Kg/Ton] of water. For comparison purposes, other set of samples was agglomerated in the same conditions, this time adding CaCl_2 dissolved in the agglomeration water, in variable proportions ranging from 2 to 10 [Kg/Ton]. That is, the agglomeration water contained between 22 and 110 [g/l] of CaCl_2 . The agglomeration took place into a rotating drum at laboratory scale, and by means of procedures that are standard in these studies. Later, the material agglomerated was loaded in columns, and their hydrodynamic properties were measured according to the procedures as developed by SMP.

The results obtained after the agglomeration and a 72 hour rest are shown in the Table below.

TABLE 2.1: HYDRODYNAMIC PROPERTIES

CaCl_2 added [Kg/Ton]	0	2	6	10
Liquid permeability [D's]	500	450	610	730
Gas permeability [D's]	1000	1100	1400	1700
Gas porosity (%)	23.3	25.0	26.0	28.0

(D'S) = (Darcy) : 1 Darcy = $0.987 \times 10^{-8} \text{ cm}^2$

Permeabilities are measured in Darcy's, equivalent to 10^{-8} cm^2 . The gas porosity measured corresponds to the drained column rather than during the irrigation. With these results, not optimized in this experiment, is fairly clear the advantage of the use of this salt.

In other set of tests, an ore much more altered than the previous one, with a high clay contents, was used. Ten (10) agglomerated columns in the traditional way, and 10 columns with a calcium chloride contents corresponding to 10 Kg/Ton, were loaded. The result showed that only the columns containing calcium chloride did not flood.

2.2.2 Leaching Sulfides in the Agglomeration

It is known that during the normal agglomeration of mixed or sulfide copper ores, a small part of the sulfide species can be recovered, which depends on the amount of sulfuric acid added. It is believed that said recovery is due to the presence of a small proportion of ferric ion extracted in that way from the ore, by the acid reactivity. The mass balances seem to corroborate this statement.

In those cases, most of the sulfuric acid added is consumed by the gangue and the soluble copper. The consumption by the gangue, in turn, is divided into consumption for cation dissolution, and consumption for reaction with calcareous species causing the calcium to precipitate.

Figure 2.1 shows the distribution of the acid consumption for a typical ore agglomerated in the traditional way, based on the quantity, in [Kg/Ton] of acid added. As it can be seen, the acid consumed by the cations monotonously increments with the acid added, while the consumption by the calcium tends to a constant value as the amount of acid added increments. This is due to the formation of a calcium sulfate layer around the calcareous particles, preventing a stronger attack. On the other hand, the copper extraction increments very quickly with low additions of acid, but it also tends to a constant value with higher additions, indicating that there exist a preferential attack of the sulfuric acid on the cations more common for the high levels of acid.

The unexpected result above mentioned, obtained when adding CaCl_2 to the agglomeration, is clearly seen when performing a test similar to the previous one but in the presence of this salt. Figure 2.2 was obtained by agglomerating the same ore in the previous test, with a constant amount of sulfuric acid, but now changing the amount of calcium chloride in the water added, from 0 to 13 [Kg/Ton]. As it can be seen, the addition of chloride has an important effect.

The acid consumption due to the extraction of the cations forming the “impurities” of the gangue decreases, indicating a lower extraction by the cations, while the attack on the calcareous gangue keeps constant, however, the acid consumption due to the copper extracted significantly increases, indicating a higher extraction, in this case, of nearly two times.

The most surprising, however, is analyzing the solid wastes of these agglomerations. The Table No 22 shows the copper recoveries: soluble ones, and insoluble ones, as obtained for the same previous tests.

TABLE No 2.2: COPPER RECOVERY BY ADDING CaCl_2

CaCl_2 [Kg/Ton]	0.00	2.84	5.59	8.25	10.73	13.04
Rec. CuS [%]	45.41	48.51	43.85	34.27	26.84	19.15
Rec CuI [%]	5.91	9.58	15.63	22.11	27.11	33.12
Total Rec [%]	16.46	19.98	23.17	25.36	27.04	29.39
[CL] Soaking [g/l]	0.0	20.7	40.8	60.3	78.4	95.3

Unexpectedly, the insoluble copper recovery has significantly increased based on the amount of salt added, while the soluble copper recovery has decreased. However, there exist a net increment in the total copper recovery.

This situation is opposed to what happens in a normal agglomeration, where the soluble copper extraction is based on the amount of sulfuric acid added, while that of insoluble copper remains constant.

For the purpose to find an explanation to this phenomenon, a similar test was conducted, this time using sodium chloride rather than calcium chloride. The sodium chloride does not react during the agglomeration stage. Its single role is, in this case, contributing sodium and chloride ions. Furthermore, in this case, the chloride ions do not replace the sulfate ions, as in the previous case, but they simply add to them.

There is no a reason, in this case, for the sodium chloride to behave as agglomerating agent.

The Figure 2.3 and the Table 2.3 show the results obtained in this case, as can be easily seen, they are very similar to the previous test.

TABLE No 2.3: COPPER RECOVERIES BY ADDING NaCl

CaCl ₂ [Kg/Ton]	0.00	3.53	6.84	10.12	13.64	13.96
Rec. CuS [%]	40.54	35.15	21.48	23.41	30.62	19.15
Rec Cul [%]	9.05	16.36	15.63	26.78	31.41	32.32
	17.47	21.38	23.79	25.88	31.20	30.26
Total Rec [%]						
[CL] Soaking [g/l]	0.0	24.2	47.4	70.1	94.5	96.7

In the two tables, the concentrations of the chloride ion in the agglomerate soaking have also been added.

These results clearly show that the responsible for this behavior in the dissolution of the sulfide copper of these systems is the chloride ion. This is related to the oxidation mechanism of the copper sulfides, as discussed under point 1.3.2. In fact, this behavior is attributed to the fact that, in the presence of Cl, the formation of a reaction product, S^o, which is permeable to the oxidizing element, Fe⁺³, thus allowing the oxidation of the sulfide to continue. This effect is higher, the higher is the chloride concentration.

Now, in this process, the amount of Fe^{+3} consumed by the oxidation of the copper sulfides is much higher than the amount that can be obtained from the ore, and is given by the sulfide copper extraction in a normal agglomeration. This means that, to be able to explain the phenomenon observed, the Fe^{+3} ion should have been continuously forming during the curing, through oxidation with the air.

This is also related to the chloride ion, as shown below.

2.2.3 Oxidation of the Solutions during the Agglomeration

All agglomerates contain a certain amount of water around the ore particles, which soaks them, and forms liquid bridges among them, what is usually referred to as soaking of the agglomerate. When ore is attacked, said soaking turns into a concentrated solution containing all the ions extracted from the ore. Since the level of soaking is relatively low, usually between 60 and 90 [l/Ton], the ion concentration is generally very high.

These solutions are susceptible to get oxidized with the oxygen in the air, nevertheless, in a normal agglomeration, that is, the oxidation of the ferrous in a sulfate medium, it is generally very low, as seen in point 1.3.3. So, in this system, when the ferric ion from the ore is consumed, the dissolution of the sulfide copper practically stops.

A simple calculation proves this fact. If the oxidation rate, as we have already seen, is 0.01 g of O_2 /Hr per liter of solution (Table No 1.1), and assuming a wetness contents of 0.1 liter of solution per Kg of ore, this gives 0.001 g of O_2 /Hr per Kg of ore. Now, the global stoichiometry of the copper solution is the following:



That is, the copper production rate is about four times higher than the oxygen consumption, that is, 0.004 g of Cu^{+2} /Hr per Kg of ore.

This is also equal to 0.095 Kg of Cu^{+2} /day per Ton of ore, that is, at 0.01% extraction per day approximately, or for an ore with 1.5% of sulfide copper grade, a 0.6% daily recovery. This is a negligible amount for the agglomeration process, whose curing period is of 1 to 2 days.

This is completely different when considering the Cu^{+} oxidation in a chloride medium, where, as we have already seen, the oxidation rate can be 300 times the previous value, that is, 3% extraction in a day. This value is above the insoluble copper grades of normal ores. Since in the results as shown above, not all the insoluble copper is recovered in the agglomeration, it means that, in a chloride medium with the presence of copper, as in this case, the oxidation of the solutions is not the controlling stage for the leaching of sulfides in the agglomeration stage.

Therefore, this proposal states that the solution formed by mixing chloride – sulfate ions in the presence of cuprous and ferric ions has, in itself, an oxidation capability more than enough to meet the requirement of the sulfide oxidation. The following test is aimed at proving this statement.

The oxygen consumption rate of a solution, or an agglomerate, can be determined on an experimental basis by means of an equipment called Micro OXIMAX, which is widely used in microbiology to measure the bacterial respiration.

To determine the oxidation rate of an agglomerate in a chloride-sulfate medium, the following experiment was conducted. First, an agglomeration was performed in the following conditions: 15 [Kg/Ton] of CaCl_2 in 90 [l/Ton] of water, and 30 [Kg/Ton] of sulfuric acid. Once the agglomerate was formed, it was placed into the OXIMAX and the measurement of the consumption of oxygen based on time began nearly immediately. Figure 2.4 shows the result obtained.

The rates are expressed in ($\mu\text{g/g}\cdot\text{Hr}$), that is, oxygen oxidation rate per gram of agglomerate. Since the wetness contained in the agglomerate is 0.09 (l/Kg), to get an approximate value in [$\text{g/l}\cdot\text{Hr}$], the value of the graphic should be divided 100 times.

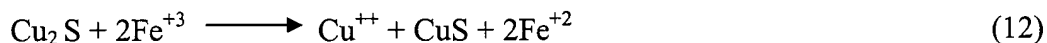
The graphic shows a very special curve. It starts with a value unusually high, and increasingly decreases with time, being the initial consumption rates sometimes higher than those established for the cuprous oxidation in a chloride medium.

For comparison purposes, the result obtained for an agglomerated identically originated, but without calcium chloride, that is, a normal agglomeration, has been illustrated in the same figure. The difference obtained is outstanding.

At this point, it is interesting to remember that the maximum oxidation rate of an agglomerate colonized by bacteria is 20 ($\mu\text{g/gHr}$), as mentioned in point 1.3.3.

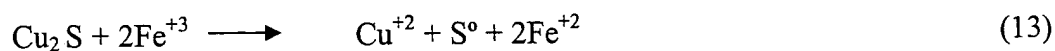
With these results and taking into account the bibliographic information, the phenomena taking place in the new agglomeration process and the subsequent rest, in relation to the copper sulfides, can be explained by means of the following mechanism:

In first place, the oxidation of the calcosine with the ferric ion is started, leaving CuS as the reaction product. This reaction is very fast provided the ferric ion is present:



In a normal sulfate medium, this ferric is rapidly consumed, and the calcosine leaching is only partial, like in a normal agglomeration.

It there is enough ferric ion in the solution, the coveline oxidation is started, which is obtained as a product of the reaction (12) or of the natural coveline:



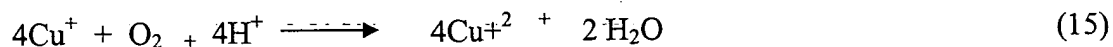
In the presence of chloride, the cupric ion is able to partially oxidize the ferrous ion, according to:



This reaction corresponds to a thermodynamic balance, that is, the reaction stops for a set of concentration values of the four ions, depending on the balance constant. On the other hand, the balance constant depends on the chloride concentration, this is due to the formation of complexes of these ions with the chloride. The reaction (14) can be descripile in several ways, depending on the complex as considered. In general, the more higher the chloride complexes, the higher is the balance constant.

However, the reaction (14) will dynamically shift to the right if, due to the process effect, the concentrations of the cuprous and ferric ions decrease.

This is what really occurs. On one hand, the ferric ion oxidizes back more sulfides according to reactions (12) and (13), and on the other hand, the cuprous ion oxidizes easily, thanks to the oxygen in the air, according to:



reaction that, as we have already seen, is very fast in the presence of chloride.

The cupric ion formed in this reaction along with the ferrous ion, formed in the oxidation reactions of the sulfides, react back according to reaction (14), again generating the ferric and cuprous ions, and repeating the same cycle. This way, this set of reactions form a self-generated, and apparently endless, oxidation system.

Since the oxidation reaction of the ion is very fast, as clearly shown by the first values in Figure 2.4, the balance reaction (14) is determined by the capability of the system to produce the ferrous ion, that is, by the oxidation rate of the sulfides, reactions (12) and (13).

This means that, what is seen in Figure 2.4 is, in fact, the sulfide oxidation rate. This is very fast at the beginning, and gradually decreases as the diffusion of the ferric ion in the particles gets slower.

In this analysis, the ferric ion has been selected as the intermediate electron acceptor. This makes sense in the current system for electro-chemical reasons. However, in no way denies the possibility that the Cu^{++} also simultaneously acts as acceptor when the presence of Cu^+ is feasible, like in the cupric chloride leaching. However, the conclusion are not changed at all.

The reactions descripile for the agglomeration only stop when the acid required for the reaction (15) is consumed. During all this process, the acid has being consumed, not only by this reaction, but also by the gangue and the soluble copper.

The Cu^+ oxidation reaction is so strong that it consumes any rest of acid left in the agglomerate. This total acid consumption also accounts for the decrease in the soluble copper as reported above. In fact, the pH of the soaking solution can be incremented by the consumption represented by the previous reactions to the extent that hydrolysis reactions begin producing. In particular, it has been found out that copper precipitates to a type of oxychloride: $\text{CuCl}_2 \cdot (\text{OH})_2$, mixed with the ferric ion in the form of a hydrosulfate: $\text{Fe}(\text{SO}_4)(\text{OH})$.

2.3 The Leaching Process

Once the fine crushed ore has been agglomerated in the presence of calcium chloride, and a part of the soluble and insoluble copper has been recovered in the curing stage, the copper extraction should continue in a leaching pile. The purpose is continuing, in the same way, the reactions started in the agglomeration.

For this to be possible, especially for the reaction balance to exist (14), the following should be present: iron, copper, and mainly chloride to allow the presence of the cuprous ion. The amounts required of these elements, which should be present in the leaching, depend on the ore being treated and determining it is the most relevant fact in the optimization of the process.

The experiments as conducted so far, for a few ores, show that the copper concentration should range from 0.5 and 10 [g/l], the iron, whether ferrous or ferric, in a value above 15 [g/l], and the chloride in a value ranging from 80 to 130 [g/l]. This chloride level is achieved in the plant balance, for example, with the addition of 10 to 20 [Kg/Ton] of calcium chloride in the agglomeration. Value likely to be reduced if saline water, or sodium chloride is used to complete the concentration. These values are similar to those found in the agglomeration soaking.

The reactions taking place during the leaching are the same descriptive for curing. However, in this case, some troubles rise for them to be fully obtained. The first of them refers to a point already discussed, and related to the oxygen transference in the agglomerate pile.

During the agglomeration and the subsequent rest or curing, the oxygen is practically available with no restrictions for the oxidation reactions. In a pile, as already analyzed, this is not necessarily true. The quality of the agglomerate determines the availability of oxygen in a pile.

This means that the reactions describable for the agglomeration take place only in the upper zone of the pile, where oxygen is available for the oxidation of the cuprous ion. The length of this zone is determined by the quality of the agglomerate.

From that point downwards, only ferric ion consumption takes place. The balance reaction (14) continues to be valid even though in the absence of oxygen. The reaction shifts to the right for ferric consumption and generation of cupric due to the copper extraction, however, the availability of the ferric ion is increasingly lower, as it gets deeper in the pile, because the generation of cupric ion by copper sulfide generation is much lower than that due to the oxidation of the cuprous ion.

Therefore, it is very important that the oxygenated zone to be as deep as possible, for the oxidation of the cuprous ion to take place.

Regarding this point, it should be stressed that, even though as discussed in the point related to the sulfide agglomeration in the leaching, the sodium chloride produced an effect similar to that of the calcium chloride, at experimental level it has been found out that, without addition of calcium chloride, the quality of the agglomeration obtained by adding only sodium chloride deteriorates over time, and can lead to the flooding of the piles. Therefore, the addition of sodium chloride in the agglomeration can be implemented only if calcium chloride is added, at the same time, as agglomerant.

The second issue is related to the copper precipitate already mentioned. In fact, the precipitate formed during the agglomeration continues forming at the pile during the first irrigation days, due to the high pH reached at that moment. From then on, it should begin dissolving, for which acid is required. However, the oxidation reaction also requires acid, so a kind of competition takes place between all the reactions for using the acid available. The oxidation reaction of the sulfides is so fast in this case, than the same, along with the consumption of gangue, reduce the availability for the precipitate dissolution. The only way of solving this is adding more acid to the leaching solution, even running the risk of causing an acid build-up at the plant. Failing to do so may affect the recovery of soluble copper. It is obvious that each type of ore, mainly its chemical and mineralogical properties, will determine the adequate treatment.

3. PREFERRED REALIZATION OF THE INVENTION

All the ideas expounded hereby translate into a set of very simple operational steps which, for a typical process to treat mixed or sulfide copper by leaching, can be summarized as follows:

- Crushing the ore to be leached at typical particle sizes: -19.05mm, -17.7mm, -9.525mm, -6.35mm, or -4.76mm, preferably in a closed circuit.
- Agglomerating the fine crushed ore, adding a CaCl_2 solution in water, and sulfuric acid. The amount of calcium chloride must be enough to obtain an agglomerate stable over time. This typical value ranges from 5 to 25 [Kg/Ton]. When the lowest value is used, the rest of the chloride to reach a balance concentration, which must be 100 [g/l] approximately, can be made up with sea water, saline water, or sodium chloride.
- Allow the agglomerate to rest as required for the oxidation reactions of the sulfides to take place. Generally, between 24 and 72 hours.
- Pile leaching the agglomerate obtained in the operation above, with a solution ranging from 80 and 130 [g/l] of chloride, over 15 [g/l] of iron, and from 0.5 to 10 [g/l] of copper. The best method to obtain this solution consists in recirculating the solution fed, and obtaining these concentrations by means of the equilibrium balance of the plant solutions.
- Washing the pile with a raffinate solution with an acid concentration of 20 [g/l], to remove the copper in the soaking, and completing the dissolution of the copper precipitates.
- Obtaining the copper from the solutions by means of the techniques already known in this matter.

This process can be obviously applied in the design of a new plant, however, it also may be applied, with few variations, to pile leaching plants currently in operation. This is especially advantageous, for example, in plants that are currently treating oxidized ores and should be modified to be able to treat mixed and sulfide ores.

One of the more obvious advantages of this process is its capability to use saline waters, or ores containing chloride, which is one of the main limitations of the bacterial leaching. In our country there are several plants facing this problem, as well as there are others consuming H_2O for agricultural use, having saline waters nearby.

All the steps listed above can be implemented by means of the flow diagram as shown in Figure 3.1, which is one of the preferred realizations of the invention.

In it, the fine crushed ore is agglomerated, and then leached with a recirculation solution. Part of the solution fed is solvent extracted, and the raffinate solution obtained is used to wash the pile in the final stage. In this system, all the chloride added to agglomerate is removed in the final wastes.

An improved version of the preferred realization is shown in the flow diagram in Figure 3.2, consisting in a process to regenerate the calcium chloride. In this case, part of the raffinate flow is removed from the recirculating system and mixed with calcium chloride. The reaction, taking place until getting completely consumed, consists in precipitating all the sulfate ion contained in the raffinate, as calcium sulfate, leaving the chloride anion in solution only. Once filtered, this solution containing all the cations as well as the chloride anion, is neutralized with lime. Said neutralization makes, thanks to a pH rise, all the cations to precipitate, except the calcium Na and K.

This precipitation can take place in fractions, if desired, to obtain cation pure compounds, such as Al, Mg, and Fe Hydroxide, which can be commercially valuable. There exist an industrial process⁴⁰ supporting this possibility.

Following a new filtering, the final solution consists in a pure calcium chloride solution, a part of which is used to precipitate plaster with the raffinate, and another part is returned to the agglomeration stage as fresh calcium chloride.

This way, calcium chloride is regenerated by only consuming lime and the acid extracted from the raffinate flow. In this realization of the invention, the system just requires calcium chloride to replace the normal losses of the process, in the spent ore, and the filtering soaking. If sea water is used, saline water, or sodium chloride, this latter element does not precipitate and keeps a constant value throughout the process.

4. APPLICATION EXAMPLE

Even though a series of experiments with various materials has been conducted since the submission of the provisional patent petition, the results as obtained in one of the cases will be expounded, stressing that nearly the same level of success has been obtained with all of them.

An ore, whose copper mineralization consisted in: 64% of calcosine; 0.5% of coveline; 5.3% of chalcopryrite; and, 29.4% of bornite, with a chemical analysis given by:

Total Cu	:	1.872%
Soluble Cu	:	0.525%
Insoluble Cu	:	1.347%

and with an acid consumption test of 55.74 [Kg/Ton] of sulfuric acid (average consumer type) was agglomerated with water containing 20 [Kg/Ton] of CaCl_2 and 30 [Kg/Ton] of sulfuric acid, into an agglomeration drum, and left resting for 48 hours.

Two duplicated columns of 203.2 mm, 3 meter high, were fed with this material, and irrigated at a rate of 0.3 [lts/min/m²]. The irrigation solution composition was the following:

Cu^{+2}	:	3.30	[g/l]
FeT	:	35.70	[g/l]
Fe^{+2}	:	24.79	[g/l]
Al^{+3}	:	17.30	[g/l]
Mg^{+2}	:	24.00	[g/l]
Mn^{+2}	:	5.5	[g/l]
SO_4	:	151.48	[g/l]

Both columns were irrigated for 110 days. These experiments did not include flushing. Once leaching was completed, the columns were unloaded in 5 fractions based on the height, to determine the presence of a potential segregation.

The results obtained are shown in Figures 4.1 to 4.4. Figure 4.1 shows a comparison of the recoveries against those corresponding to a bacterial leaching. Figure 4.2 shows the total copper recovery per height fractions.

It is interesting observing the high recovery as obtained in the first 10 days of leaching. This is undoubtedly due to the reactions occurred in the agglomeration. This fact allows obtaining a recovery higher than the bacterial one, in less than half of the time.

On the other hand, the height segregation is not significant after the 110 days.

Figure 4.4 shows the soluble copper recovery. This recovery is lower than expected. This is due, as proved in subsequent experiments, to the copper precipitate as obtained by the agglomeration. Said precipitate can be extracted in two ways: On one hand, by increasing the leaching acid concentration, and on the other hand, by washing with a high acid contents raffinate, which was not implemented in this example.

The following table shows the values

illustrated in Figure 2.1

CURING VARIABLE

CURING VARIABLE										
WITH 10 K/T CaCl ₂ ACID EFFECT										
SAMPLE	ORE	ESTEFA NIA	-y 4 - F2 Fann			DESTILLED WATER				
SIZE	-3/8"					Acid Density	1,83	[g/cm ³]		
TIME FRAME	72 Hours					CaCl ₂ nominal	10,0	[Kg/To n]		
EXPERIMENT		1	2	3	4	5	6	7	8	9
Acid in Curing	[Kg/To n]	0	10	20	30	40	50	60	70	80
CHARACTERIZATION OF THE SAMPLE										
CUT	1%]	2,940	2,758	2,926	3,003	3,086	3,142	2,873	2,987	3,065
CuS	1%]	1,256	1,178	1,250	1,283	1,318	1,342	1,227	1,276	1,309
CuI	(%)	1,684	1,580	1,676	1,721	1,768	1,800	1,646	1,711	1,756
%CuS	1%]	42,7	42,7	42,7	42,7	42,7	42,7	42,7	42,7	42,7
FeT	1%)	5,110	5,421	5,167	5,514	6,28	5,774	6,388	-6j224	6,368
FeS	1%]	0,400	0,431	0,447	0,574	0,797	0,944	1,428	1,284	1,618
FeI	1%)	4,710	4,990	4,720	4,940	5,490	4,830	4,960	4,940	4,750
%FeS	1%]	7,8	8,0	8,7	10,4	12,7	16,4	22,4	20,6	25,4
C Ac	[Kg/To n]	54,73	54,73	54,73	54,73	54,73	54,73	54,73	54,73	54,73
% Wetness	1%]	0,830	0,830	0,830	-0,830	0,830	0,830	0,830	0,830	0,830
CURING CONDITIONS										
Acid	[Kg/To n]	0	10	20	30	40	50	60	70	80
CaCl ₂	(Kg/To n]	10	10	10	10	10	10	10	10	10
Salt	[g/l]	523	523	523	523	523	523	523	523	523
M Min. Wet.	[g]	4.650	4.850	4.700	4.700	4.850	4.700	4.550	4.600	4.700
V, Solution	[cm ³]	88	92	89	89	92	89	86	87	89
V, Acid	[cm ³]	0	27	521	78	1071	130	152	178	208
V, Additional Water	[cm ³]	214	223	216	216	223	217	210	212	217
M, Total	[g]	4.998	5.263	5.147	5.194	5.409	5.290	5.169	5.270	5.433
RESULTS										
RECOVERIES:										
CUT	[%]	11,6	19,9	23,1	27,4	29,7	30,0	32,5	31,7	35,4

CuS	[%]	26,1	22,7	36,0	37,6	39,3	50,1	38,9	42,0	46,5
CuI	[%]	1,4	17,7	13,5	19,8	22	15,0	27,7	24,0	27,1
CuS r	(%)	29,1	33,0	46,7	51,4	52,2	49,6	58,3	30,7	48,3
CuPp/CuS	[%]	4,0	10,2	10,7	13,8	12,9	-0,5	19,4	-11,3	1,8
Cons Ac Cu	[Kg/To n]	5,25	8,46	10,44	-12,71	14,14	14,54	14,41	14,152	16,75
Cons Imp	[Kg/To n]	1,40	2,55	5,68	12,87	20,05	28,88	38,76	44,51	56,97
Cons Pp	[Kg/To n]	-1,55	4,21	7,14	-6,07	5,84	6,85	2,47	6,73	-4,04
Cons total	(Kg/To n]	5,10	15,22	23,21	31,65	40,03	50,27	55,64	65,86	69,69
SO4=Pp	[Kg/To n]	0,91	6,77	10,09	8,86	8,86	9,66	, 6,26	10,67	0,09
FeT Gen	[Kg/To n]	0,10	0,21	0,67	2,14	3,87	5,74	7,88	9,24	11,68
Fe+3 Gen	[Kg/To n]	0,46	5,01	4,09	5,24	5,32	2,44	4,73	4,49	5,27
Fe+2 Gen	[Kg/To n]	0,43	4,93	3,98	-5,igg	7,00	4,75	8,02	7,23	8,37
Cl-	[Kg/To n]	6,53	7,31	7,26	6,65	7,40	7,01	6,14	5,67	6,25

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CLAIMS

1. Procedure to agglomerate fine crushed copper ores forming piles with liquid permeability, over non-flooded pile, above 200 Darcy, and gas permeability, over non-flood pile, above 1,000 Darcy, Comprising the steps of:
 - a) in the agglomeration stage, a first solution containing calcium chloride is added, in a proportion of 5 to 25 kilograms of calcium chloride per ton of ore, in concentrations ranging from 22 to 110 grams of calcium chloride per liter of solution;
 - b) in the agglomeration stage, a second solution containing sulfate ion is added, in a proportion of 5 to 80 kilograms of sulfate ion per ton of ore, in concentrations ranging from 150 to 1,800 grams of ion per liter of solution;
 - c) the final agglomerate has a water contents ranging from 35 to 130 kilograms per ton or ore;
 - d) in the agglomeration stage, a water flow is added when the combination of the first and the second solutions does not comply with the range in point c).
- 2.- Procedure to agglomerate fine crushed copper ores, according to claim No 1 wherein the aqueous solution containing the calcium chloride is formed with pure or industrial water, or sea or saline water
- 3.- Procedure to agglomerate fine crushed copper ores, according to claim No 1. wherein: the solution containing sulfate ion is sulfuric acid, with a concentration ranging from 14% to 98 % in weight.
- 4.- Preferred procedure to leach liquid permeability piles, over non-flooded pile, above 200 Darcy, and gas permeability, over non-flooded pile, above 1,000 Darcy of fine crushed copper ores agglomerated according to claim No 1, comprising the steps of:
 - a) a pile of agglomerated ore is formed, and allowed to rest for a period ranging from 1 to 120 hours;
 - b) the pile is leached by means of a flow of leaching solution ranging from 5 to 100 [l / (m² x hr)] for a period between 1 and 200 days.
 - c) the leached pile is flushed with a flow of solution ranging from 5 to 100 [l / (m² x hr)] for a period between 1 to 10 days.

- 5.- Procedure to leach piles, according to claim No 4, wherein:
the solution contains between 0.5 and 10 [g/l] of copper, between 80 and 130 [g/l] of chloride, between 15 and 40 [g/l] of total iron, and between 1 and 20 [g/l] of equivalent sulfuric acidity.
- 6.- Procedure to leach piles, according to claim No 5, wherein:
the leaching solution is composed of intermediate solutions of the process.
- 7.- Procedure to leach piles, according to claim No 5, wherein: the whole or part of the chloride in the leaching solution is contributed by the calcium chloride used as agglomerant.
- 8.- Procedure to leach piles, according to claim No 4, wherein the washing solution is pure or industrial water, or sea, saline, or raffinate water.
- 9.- Procedure to leach piles, according to claim No 8, wherein the raffinate contains between 0 and 1 [g/l] of copper, between 60 and 130 [g/l] of chloride, between 0 and 10 [g/l] of total iron, and between 10 and 40 [g/l] of equivalent sulfuric acidity.

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